



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: Activation of small molecules on perovskites- correlation between dopants, structural defects and reactivity

Experiment number: MA 5350

Beamline:	Date of experiment: from: 05/04/2022 to: 12/04/2022	Date of report: 20/07/2022
Shifts:18	Local contact(s): Pieter Glatzel	<i>Received at ESRF:</i>

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Report

Abstract: This proposal aims to study the local structure of Pt particles dispersed on $\text{CaTi}_{1-x}\text{Fe}_x\text{O}_{3-d}$, with $x=0, 0.1, 0.2, 0.3, 0.4, 0.7$ during CO oxidation. This novel support material shows catalytic activities similar to ceria, converting CO already at room temperature. We believe that this high performance is due to the presence of both, Ti and Fe in the support and interaction with Pt and the support, via oxygen vacancies created through Fe-doping and/or strong metal-support interaction (creation of Pt-Fe bonds). Using operando photon-in/photon-out spectroscopy we will study the electronic structure and local coordination of Ti, Fe and Pt.

Description of the experiment: We opted for a mixed configuration of different crystal analysers in order to be able to probe the different edges present in the Pt-CTF catalyst (Fe, Ti K-edge and Pt L_{3-} edge) during the *in-situ* and operando experiment. The sample was sieved and put in 1.5mm quartz capillaries. The inlet was connected to a mass flow controller system and the outlet to a mass spectrometer. The heating of the sample was performed using a gas blower.

In the first part of the experiment the Pt-CTFX samples (with $x = 0.1, 0.4$) were measured ex-situ as pellets at RT. Then we proceeded with the *in-situ* experimental protocol: activation of the catalyst under H_2 at 350°C cooling down at RT (step1). Subsequent fast flush in He, and heating of the catalyst up to 250°C in CO oxidation gas feed conditions (nominally 1000ppm CO and 10 000 ppm O_2). Each sample was then cooled down to a suitable temperature (about 160°C) sufficient to see both CO and CO_2 signal in the mass spectrometer. At this temperature we measured the sample in $\text{CO}+\text{O}_2$ (step 2), O_2 (step 3), $\text{CO}+\text{O}_2$ (step 4), CO (step 5), and again in $\text{CO}+\text{O}_2$ (step 6), probing both the Pt nanoparticles and the Fe and Ti atoms in the CTF support material in reducing and oxidizing conditions. The duration of the protocol for each sample was about 21h.

Results:

The ex-situ measurements spectra show that all sample the Pt nanoparticles are oxidized (very high white line intensity compared to Pt reference foil). All the Ti spectra are really close each other the main difference lays in the pre-edge region where the intensity of the t_{2g} feature (4.968-4.971 keV) increases along with the increasing of the Fe doping while the e_g (4.973-4.976 keV) is decreasing (Fig. 1 green box top figure). From the Fe K-edge XANES we observe the presence of just one pre-edge features at 7.14 -7.15 keV which we link to the sole presence of Fe(III) in the system. Moreover, we

observe the presence of a small shoulder on the rising edge region which might be related to the presence of oxygen vacancies/mobility in the system as will be explained later. A direct comparison of the Fe-XANES spectra between different samples result difficult because of the presence of strong self-absorption (increase of the pre-edge intensity and decrease of the white line intensity). Thus all the comparison between spectra has been done qualitatively (Fig. 1 green box bottom figure).

From the *in-situ* measurements the following preliminary results can be given:

Under activation conditions (step 1) the white line of the Pt L₃ XANES nanoparticles decrease, which is an indication of the reduction of the Pt nanoparticles (Fig. 1 a,d blue lines). The Ti sites, as expected, are not reduced, indeed XANES and XES Ti K-edge spectra in this condition do not show any change from the ex-situ spectra. Conversely, the XAS and XES Fe K-edge a notable shift at lower energies in the XANES rising edge region (Fig. 1 b, e, blue lines) is appearing and a small shift in the crossover peak at 7.093 keV (Fig. 1 c, f, blue lines) in the valence to core (vtc) XES compared to the ex-situ spectra. We attribute these changes as the evidence of O₂ depletion from the CTF bulk to participate into the oxidation of CO. In presence of CO+O₂ (oxidative condition, step 2, Fig 1 a,d orange line), the XANES of the Pt L₃ shows a white line intensity between the one of the ex-situ (oxidized Pt) and reduced Pt (in H₂). The Ti XANES and XES spectra do not change and won't be discussed any longer, since we were not able to detect any spectral differences. The XANES and XES Fe spectra show the same profiles of the ex-situ one. Probably during this step, the support bulk oxygen atoms are less needed (energetically disfavoured) for the reaction and/or on the other hand an equilibrium has been reached between O₂ from the gas phase and bulk oxygen. In presence of sole O₂ (step 3), the white line of the Pt XANES increases again but the XANES profile is different from the ex-situ one. We hypothesize the formation in this step of PtO₂ species. The Fe K-edge spectra do not change from the previous step. Sending again CO+O₂ (step 4) provoke similar spectral changes on the Pt L₃ spectra. The main difference here is an increase of the white line intensity respect to the spectrum in step 1 (Fig1, a,d red vs orange lines) that can be reasonably attributed to a larger presence of PtO₂ sites created once O₂ was sent. Again here, both XANES and XES Fe K-edge spectra do not change. Switching to sole CO (reducing conditions, step 5) we see again a strong decrease of the white line in the Pt XANES, while the Fe XANES and XES spectra show the same changes in the rising edge and crossover peak region as in the case of H₂ reduction. In this condition it is easier to assert that these changes really due to oxygen depletion inside the bulk of CTF support since no oxygen is provided to oxidise CO. Finally, sending for the third time CO+O₂ (step 6) causes an increase of the intensity of the Pt XANES white line, which however is lower in intensity if compared to CO+O₂ condition in step 2 (Fig1, a,d brown vs orange lines). Since CO is a strongly reducing agent we attribute this change to the presence of strongly bounded CO molecule absorbed on Pt atoms.

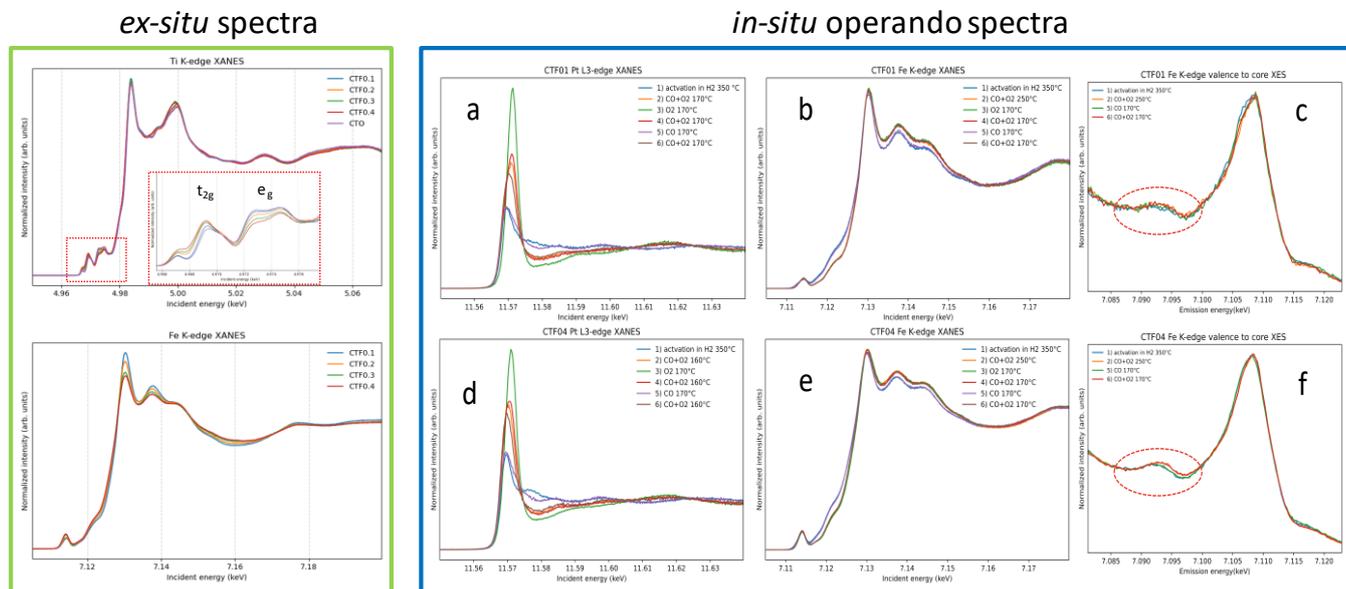


Figure 1: Green box: *ex-situ* spectra of Pt/CTFX catalyst measured as pellets (top Ti K-edge XANES, bottom Fe-K-edge). Blue box: *in-situ operando* spectra of Pt/L3 edge (a,b), Fe-K-edge XANES (b,e) and Fe K-edge vtc XES (c, f) for the two measured compositions CTF0.1 top and CTF0.4 bottom during the different experimental step (number 1 to 6). The crossover peak is highlighted with a red dashed circle.

Conclusions:

- The increase of Fe concentration in the support material do not seem to affect the reaction mechanism in the X range 0.1 to 0.4.
- The Ti atoms do not seem to participate during the reaction conditions since we do not detect any spectral change compared to the *ex-situ* spectra.
- XANES and XES seems to be suitable tools to distinguish the speciation of the Pt nanoparticles and detect the oxygen mobility. However, further investigation has to be made to properly assert this point. (XANES and XES ab-initio calculations will be crucial).

- It is clear that Fe doping allows oxygen mobility but unfortunately its role is still not fully understood since no clear chemical oxidation or reduction has been observed.